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Toshihito MIYAMA *et al.*
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For: PROTON CONDUCTING MEMBRANE, METHOD FOR PRODUCING
THE SAME AND FUEL CELL USING THE SAME

STATEMENT

Commissioner for Patents
Alexandria, VA 22313-1450

Sir/Madam:

I, Hidetaka Ota, residing at Toranomon East Bldg., 8F, 7-13, Nishi-Shimbashi 1-chome, Minato-ku, Tokyo, Japan hereby state that:

I well understand the Japanese and English languages and attached is an accurate English translation made by me of Japanese Patent Application No. 2003-122766, filed April 25, 2003.

Date : December 25, 2009

Name : 

Hidetaka Ota

**PATENT OFFICE
JAPANESE GOVERNMENT**

This is to certify that the annexed is a true copy of the following application as filed with this Office.

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Applicant(s): SEKISUI CHEMICAL CO., LTD.

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[Name of Article] Figure 1

[Name of Article] Abstract 1

[Necessity of Proof] Yes

[Designation of Document] SPECIFICATION

[Title of the Invention] PROTON CONDUCTING MEMBRANE,
METHOD FOR PRODUCING THE SAME AND FUEL CELL USING THE
SAME

[Designation of Document] CLAIMS

[Claim 1]

A proton conducting membrane comprising a support filled with a proton conducting structure (β) comprising an acid-containing structure containing an acid group, the support comprising an organic-inorganic composite structure (α) having a crosslinked structure formed by a metal-oxygen bond and an open-cell structure having internally-formed pores connected continuously to each other by said crosslinked structure.

[Claim 2]

The proton conducting membrane as described in Claim 1, wherein the porosity of the open-cell structure falls within a range of from 20 to 95% by volume based on the support comprising the organic-inorganic composite structure (α).

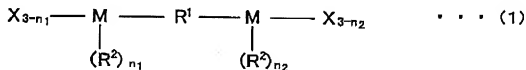
[Claim 3]

The proton conducting membrane as described in Claim 1 or 2, wherein a diameter of the pores is from 0.01 to 10 μm .

[Claim 4]

The proton conducting membrane as described in any one of Claims 1 to 3, wherein the organic-inorganic composite structure (α) comprises a structure represented by the following formula (1):

[chem.1]



(wherein M represents a metal atom; X represents -O- bond taking part in crosslinking or OH group; R^1 represents a C_1 - C_{50} carbon atom-containing molecular chain group; R^2 represents a methyl, ethyl, propyl or phenyl group; and n_1 and n_2 each represent 0, 1 or 2, with the proviso that at least one of n_1 and n_2 represents 1 or 2.)

[Claim 5]

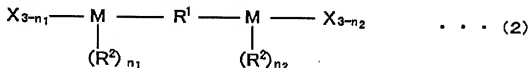
The proton conducting membrane as described in any one of Claims 1 to 4, wherein the proton conducting structure (β) includes a mixed composition comprising an organic-inorganic composite structure (βB) having a crosslinked structure formed by a metal-oxygen bond, and an acid-containing structure (βC).

[Claim 6]

The proton conducting membrane as described in

Claim 5, wherein the organic-inorganic composite structure (βB) is represented by the following formula (2):

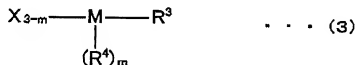
[chem.2]



(wherein M represents a metal atom; X represents -O-bond taking part in crosslinking or OH group; R^1 represents a C_1 - C_{50} carbon atom-containing molecular chain group; R^2 represents any of methyl, ethyl, propyl and phenyl groups; and n_1 and n_2 each represents 0, 1 or 2); and

wherein an acid-containing structure (βC) is represented by the following formula (3):

[chem.3]



(wherein M represents a metal element; X represents -O-bond taking part in crosslinking or OH group; R^3 represents a molecular chain group having at least one acid group; R^4 represents any of methyl, ethyl, propyl and

phenyl groups; and m represents 0, 1 or 2.)

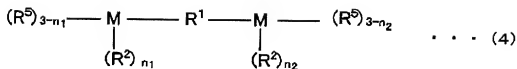
[Claim 7]

A method of producing a proton conducting membrane, wherein the organic-inorganic composite (α) having a crosslinked structure is produced by a step of preparing a mixture containing an organic-inorganic composite crosslinkable compound (A) terminated by at least one crosslinkable silyl group and a carbon atom covalently connected thereto, a step of forming said mixture into a film and a step of subjecting the crosslinkable silyl group contained in the mixture thus film-formed to hydrolysis and/or condensation; subsequently filling mixture of an organic-inorganic composite crosslinkable compound (B) and an acid containing compound (C) in the organic-inorganic composite structure (α), to subject the crosslinkable silyl group contained in the filled mixture to hydrolysis and/or condensation, thereby forming a crosslinked structure of a proton conducting structure (β) in the organic-inorganic composite structure (α).

[Claim 8]

The method of producing a proton conducting membrane as described in Claim 7, wherein the organic-inorganic composite crosslinkable compound (A) is represented by the following formula (4):

[chem.4]



(wherein M represents a metal atom; R¹ represents a C₁-C₃₀ carbon atom-containing molecular chain group; R² represents any of methyl, ethyl, propyl and phenyl groups; R⁵ represents any of Cl, OCH₃, OC₂H₅, OC₆H₅, OH, and OCOCH₃; and n₁ and n₂ each represent 0, 1 or 2, with the proviso that at least one of n₁ and n₂ is 1 or 2.)

[Claim 9]

The method of producing a proton conducting membrane as described in Claim 7 or 8, further comprising a step of adding a catalyst in an amount arranged such that water is present in an amount of from 0.5 to 1.5 equivalents to the crosslinkable silyl group in the organic-inorganic composite crosslinkable compound (A).

[Claim 10]

The method of producing a proton conducting membrane as described in Claim 9, wherein a Brønsted acid is used as a catalyst during the hydrolysis of the crosslinkable silyl group in the organic-inorganic composite crosslinkable compound (A).

[Claim 11]

The method of producing a proton conducting membrane as described in any one of Claims 7 to 10, further comprising a step of mixing the organic-inorganic composite crosslinkable compound (A) with a solvent in an amount of from 0.5 to 10 ml per g of the solid content of the organic-inorganic composite crosslinkable compound (A).

[Claim 12]

A fuel cell comprising a proton conducting membrane as described in any one of Claims 1 to 6.

[Detailed Description of the Invention]

[0001]

[Technical Field]

The present invention relates to a proton conducting membrane, a method for producing the same and a fuel cell using the same and more particularly to a proton conducting membrane which is excellent in heat resistance, durability, dimensional stability, fuel barrier properties, etc. and exhibits an excellent protonic conductivity even at high temperatures, a method for producing the same and a fuel cell by using the same.

[0002]

[Background Art]

In recent years, a fuel cells have been noted as a next-generation electricity-generating device which can contribute to the solution of environmental issues and energy issues, which are significant social problems, because it exhibits a high electricity generating efficiency and is excellent as a clean energy source. Particularly, the polymer electrolyte fuel cell (hereinafter occasionally referred to as "PEFC") has a small size and a high performance among fuel cells and has been regarded as a next-generation mainstream of electric supply such as small-scale on-site electric supply, electric supply for mobile body, e.g., power

source for vehicle, and electric supply for portable devices and variously researched and developed.

[0003]

A proton conducting membrane provided in such a fuel cell functions to transmit protons produced on the anode to the cathode side, and the movement of protons occurs in cooperation with the flow of electrons.

Accordingly, in order that PEFC might give a high output, i.e., high current density, it is necessary that protonic conduction be conducted at a high rate in a sufficient amount.

Further, the proton conducting membrane not only functions to conduct proton but also functions as an electrically insulating membrane of the anode off the cathode and a fuel barrier membrane that prevents the fuel supplied to the anode side from leaking to the cathode side.

As described above, it is considered that the performance of the proton conducting membrane is a key material that determines the performance of PEFC.

[0004]

The main proton conducting membrane which is now used in PEFC is a fluororesin-based membrane comprising a perfluoroalkylene as a main skeleton and having a sulfonic acid group at a portion of the end of

perfluorovinylether side chain. As such sulfonated fluororesin-based membranes there are known, e.g., Nafion (trade name) membrane (Du Pont Inc.; see US Patent 4,330,654), Dow membrane (Dow Chemical Inc.; see JP-A-4-366137), Aciplex (trade name) membrane (Asahi Kasei Corporation; see JP-A-6-342665), Flemion (trade name) membrane (ASAHI GLASS COMPANY), etc.

[0005]

Since in these fluororesin-based membranes creep occurs, the maximum temperature of present use at which the fuel cell using such fluororesin-based membranes can be stably used over an extended period of time is normally regarded as 80°C. On the other hand, since it exhibits a higher energy efficiency when operated at high temperatures, a fuel cell can be further reduced in size and weight. Further, when the fuel cell is operated at high temperatures, exhaust heat can be utilized (cogeneration: a combined supply of heat and electricity) that drastically enhances the total energy efficiency. Further, it is preferable that the operating temperature of a fuel cell is a temperature as high as possible, that is, 100°C or more, preferably 120°C or more from the viewpoint of preventing catalyst poisoning of the anode side, and reducing catalyst cost.

[0006]

In direct fuel type fuel cells, methods have been variously studied to directly and efficiently extract protons and electrons from fuel. In order to sufficiently obtain sufficient fuel cell performance, for example, regardless of the knowledge in which it is preferably to operate in high temperatures of 150°C or more, the heat resistance of the proton conducting membrane is up to 80°C the operating temperature of the fuel cell, too, is thus limited to 80°C at present.

[0007]

When the fuel cell is operated, the temperature in PEFC then spontaneously rises by exothermic reaction. However, since proton conducting membrane is so heat-resistant as to withstand up to about 80°C, it is necessary that PEFC be cooled. Such cooling is normally accomplished by water cooling. When such a cooling device is introduced at the separator portion of a PEFC, the PEFC becomes large-sized and heavy as a whole, making it impossible to use of small size and light weight, which are inherent characteristics of PEFC. In particular, when the critical operating temperature is 80°C, effective cooling is made difficult in the water cooling system, which is the simplest cooling means.

[0008]

When operation of fuel cell can be made at 100°C or

more, the heat can be utilized to evaporate water, making effective cooling, and the circulation of water makes it possible to drastically reduce the amount of water to be used during cooling and hence attain the reduction of size and weight of the device.

In the case where the fuel cell is used as an energy source for vehicle, it has been shown that the capacity of cooling water in a radiator can be drastically reduced.

[0009]

In order to raise the operating temperature of PEFC, various heat-resistant proton conducting materials have been studied and proposed to date.

A representative example of these heat-resistant proton conducting materials is a heat-resistant aromatic polymer material that substitutes for the conventional fluorine-based membranes, and examples of such a heat-resistant aromatic polymer material include polybenzimidazoles (see JP-A-9-110982), polyethersulfones (see JP-A-10-21943 and JP-A-10-45913), polyether ether ketones (see JP-A-9-87510), etc.

[0010]

These aromatic polymer materials are advantageous in that they undergo little structural change at high temperatures, but on the other hand, most of them have

sulfonic acid groups, carboxylic acid groups, etc. introduced directly in the aromatic compound, and in this case, they can undergo remarkable desulfonation or decarboxylation at high temperatures and thus are not suitable for high temperature-working membrane.

Further, these aromatic polymer materials often do not have an ion channel structure as the fluororesin-based membrane, and as a result, it is necessary that a number of acid groups be introduced to obtain sufficient protonic conductivity, raising a problem that they exhibit deteriorated membrane stability or hot water stability and can be dissolved in hot water in some cases.

[0011]

Further, when water exists, the entire membrane tends to swell remarkably as the fluororesin-based membrane does, and due to the change of the size of the membrane in drying and wet states, stress is applied to the junction of the membrane-electrode assembly, making it very likely that the membrane and the electrode can be exfoliated at the junction or the membrane can be broken, and there rises a problem that the reduction of strength of the membrane due to swelling can cause membrane destruction. Further, since all of these aromatic polymer materials are polymer compounds which stay highly rigid when dried, there rises a problem that the membrane

can undergo destruction or the like during the formation of membrane-electrode assembly.

[0012]

As proton conducting membranes there have been proposed the following inorganic materials. For example, Minami et al obtained proton conducting inorganic materials by incorporating various acids in a hydrolyzable silyl compound (see "Solid State Ionics", vol. 74, page 105, 1994). However, these inorganic materials exhibit stable protonic conductivity even at high temperatures but can easily crack when used as thin film and thus can be difficultly handled and assembled to a membrane-electrode assembly.

[0013]

In order to overcome these problems, a method which comprises grinding a proton conducting inorganic material, and then mixing the material thus ground with an elastomer (see JP-A-8-249923), a method which comprises mixing the material thus ground with a sulfonic acid group-containing polymer (see JP-A-10-69817), etc. for example have been attempted, but since these methods only involve the mixing of a polymer material as a binder with an inorganic crosslinked material, the mixture has no great difference in basic thermal properties from polymer material alone and thus undergoes structural change of

polymer material at high temperatures and does not exhibit stable protonic conductivity and high protonic conductivity in many cases.

[0014]

Further, JP-A-10-92444 reports a composite obtained by incorporating a solid electrolyte in a stretched formed porous polytetrafluoroethylene product having open cells the inner surface of which is coated with a metal oxide. However, such a composite has many producing steps and thus is complicated, and economically undesirable, and since the metal oxide conducting agent and the formed product as support i different elements, the adhesion of the conducting agent to the support is incomplete. Further, in the examples, silica gel is exemplified as metal oxide, but silica gel is poor in flexibility and thus is considered to give obstruction during subsequent working.

[0015]

Further, JP-A-2002-358979 reports a polymer solid electrolyte composite membrane comprising a porous membrane made of a metaphenylene isophthalamide-based polymer having a large number of uniform micropores formed on the surface and interior thereof and a polymer solid electrolyte material incorporated in the pores. Such a membrane is advantageous in that it enhances the

mechanical strength, but since a polymer solid electrolyte conductor made of a perfluororesin and porous support is made of different elements, it is possible to cause a problem of occurring stress in the interface due to the change of temperature in use, and stripping.

[0016]

Further, JP-A-2002-83612 reports an electrolyte membrane obtained by forming a proton conducting polymer having its one end bonded on the surface of pores in a porous substrate which swells with an organic solvent and water, and then filling a second proton conducting polymer which is the same as or different from the first polymer in the pores. In this case, it is required to perform filling process two times, and require a complicated step and thus is economically undesirable. To chemically connect the first polymer to a porous substrate, when irradiated with plasma, ultraviolet, or the like, a complicated step is required and thus it is not preferable from the viewpoint of energy consumption. As substrate material, any one of ceramic, glass and alumina or composite material thereof, polytetrafluoroethylene or polyimide is proposed. Monomer forming polymer exemplified as conducting agent includes monomer and ester derivative thereof having a vinyl group, a strong acid group such as sulfonic acid

and phosphonic acid, weak acid group such as carboxyl group, strong base group such as primary, secondary, tertiary, or quaternary amines, weak base in structure so that physical bond with support is weak.

[0017]

As described above, a support having open cells comprising a conducting agent incorporated therein is advantageous in that it enhances the mechanical strength and prevents swelling with hot water, but the stress repeatedly acts on the surface between the conducting agent, and support during the change of temperature, and it can lead to interfacial exfoliation or destruction.

[0018]

Since a conventional proton conducting membrane has insufficient flexibility, when assembling with electrode, incorporating into a fuel cell, or operating a fuel cell, the membrane easily generates breakage, which makes it difficult that not only to be used as a fuel cell membrane, but also to be obtained as a membrane having sufficient size to incorporate in a fuel cell without breakage.

[0019]

As has been mentioned above, in view of various considerations, such as electricity generating efficiency, cogeneration efficiency, cost, resource, cooling

efficiency etc., regardless of the preference for high temperature-working membranes of PEFC, that is, heat resistance of proton conducting membranes in high temperature, there have been not a proton conducting membrane combining all the physical properties such as sufficient protonic conductivity, and mechanical strength such as heat resistance, durability, and flexibility yet.

[0020]

[Problem that the Invention is to Solve]

Accordingly, an object of the present invention is to provide a proton conducting membrane which is excellent in heat resistance, durability, dimensional stability, fuel barrier properties, flexibility etc. and exhibits an excellent protonic conductivity even at high temperatures to solve problems described above in conventional polymer electrolyte fuel cells.

[0021]

Further, another object of the present invention is to provide a method of producing a proton conducting membrane which can economically and effectively produce the aforementioned proton conducting membrane of the present invention.

[0022]

Further, a further object of the present invention is to provide a fuel cell which comprises the

aforementioned proton conducting membrane of the present invention and thus can stably operate at high temperatures.

[0023]

[Means for Solving the Problem]

The present inventors made extensive studies in the light of the aforementioned problems, and as a result of studies of various electrolyte membrane materials, it was found that when a support (α) having an open-cell structure which is a crosslinked structure having a specific organic-inorganic composite structure is filled with a proton conducting structure (β) as an essential component constituting the membrane, a proton conducting membrane having excellent durability, dimensional stability, fuel barrier properties, etc. can be obtained, and the present invention has been worked out.

[0024]

In other words, in accordance with the aspect of the present invention, a proton conducting membrane comprising a support filled with a proton conducting structure (β) comprising an acid-containing structure containing an acid group, the support comprising an organic-inorganic composite structure (α) having a crosslinked structure formed by a metal-oxygen bond and an open-cell structure having internally-formed pores

connected continuously to each other by said crosslinked structure, is provided.

[0025]

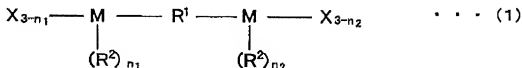
Further, in accordance with the aspect of the present invention, a proton conducting membrane as mentioned above is provided, wherein the porosity of the aforesaid open-cell structure falls within a range of from 20 to 95% by volume based on the support comprising the organic-inorganic composite structure (α).

Further, in accordance with the aspect of the present invention, a proton conducting membrane as mentioned above is provided, wherein a diameter of the pores is from 0.01 to 10 μm .

[0026]

Further, in accordance with the aspect of the present invention, a proton conducting membrane as mentioned above is provided, wherein the organic-inorganic composite structure (α) comprises a structure represented by the following formula (1):

[chem.5]



(wherein M represents a metal atom; X represents -O-bond taking part in crosslinking or OH group; R¹ represents a C₁-C₅₀ carbon atom-containing molecular chain group; R² represents a methyl, ethyl, propyl or phenyl group; and n₁ and n₂ each represent 0, 1 or 2, with the proviso that at least one of n₁ and n₂ represents 1 or 2.)

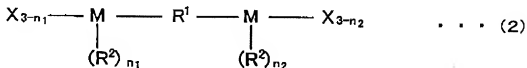
[0027]

In accordance with an aspect of the present invention, the proton conducting membrane as mentioned above is provided, wherein the proton conducting structure (β) is a mixed composition comprising organic-inorganic composite structure (βB) having a crosslinked structure formed by a metal-oxygen bond, preferably a silicon-oxygen bond and an acid-containing structure (βC).

[0028]

Further, in accordance with the aspect of the present invention, a proton conducting membrane as mentioned above is provided, wherein an organic-inorganic composite structure (βB) is represented by the following formula (2):

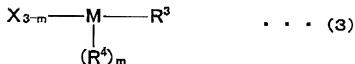
[chem.6]



(wherein M represents a metal atom; X represents -O-bond taking part in crosslinking or OH group; R¹ represents a C₁-C₅₀ carbon atom-containing molecular chain group; R² represents any of methyl, ethyl, propyl and phenyl groups; and n₁ and n₂ each represent 0, 1 or 2), and

wherein an acid-containing structure (βC) is represented by the following formula (3):

[chem.7]



(wherein M represents a metal atom; X represents -O-bond taking part in crosslinking or OH group; R³ represents a molecular chain group having at least one acid group; R⁴ represents any of methyl, ethyl, propyl and phenyl groups; and m represents 0, 1 or 2.)

[0029]

Further, in accordance with the aspect of the present invention, a method of producing a proton conducting membrane is provided, wherein the organic-inorganic composite structure (α) having a crosslinked structure is produced by a step of preparing a mixture containing an organic-inorganic composite crosslinkable compound (A) terminated by at least one crosslinkable

silyl group and a carbon atom covalently connected thereto, a step of forming said mixture into a film and a step of subjecting the crosslinkable silyl group contained in the mixture thus film-formed to hydrolysis and/or condensation; subsequently filling the mixture of an organic-inorganic composite crosslinkable compound (B) and an acid containing compound (C) in the organic-inorganic composite structure (α) to subject the crosslinkable silyl group contained in the filled mixture to hydrolysis and/or condensation, thereby forming a crosslinked structure of the proton conducting structure (β) in the organic-inorganic composite structure (α).

[0030]

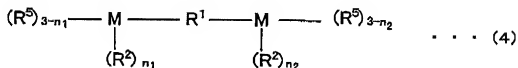
Further, in accordance with the aspect of the present invention, a method of producing a proton conducting membrane as mentioned above is provided, wherein "to have at least one crosslinkable silyl group terminated in an used organic-inorganic composite crosslinkable compound (A)" means that it is sufficient to have at least one crosslinkable silyl group in both terminals or at least one crosslinkable silyl group at one terminal.

[0031]

In accordance with the aspect of the present invention, a method of producing a proton conducting

membrane as mentioned above is provided, wherein the organic-inorganic composite crosslinkable compound (A) is represented by the following formula (4):

[chem.8]



(wherein M represents a metal atom; R¹ represents a C₁-C₅₀ carbon atom-containing molecular chain group; R² represents any of methyl, ethyl, propyl and phenyl groups; R⁵ represents any of Cl, OCH₃, OC₂H₅, OC₆H₅, OH, and OCOCH₃; and n₁ and n₂ each represent 0, 1 or 2, with the proviso that at least one of n₁ and n₂ is 1 or 2.)

[0032]

In accordance with an aspect of the present invention, a method of producing a proton conducting membrane as mentioned above is provided, further comprising a step of adding a catalyst in an amount arranged such that water is present in an amount of from 0.5 to 1.5 equivalents to the crosslinkable silyl group in the organic-inorganic composite crosslinkable compound (A).

In accordance with the aspect of the present invention, a method of producing a proton conducting

membrane as mentioned above is provided, wherein a Brønsted acid is used as a catalyst during the hydrolysis of the crosslinkable silyl group in the organic-inorganic composite crosslinkable compound (A).

[0033]

In accordance with the aspect of the present invention, a method of producing a proton conducting membrane as mentioned above is provided, further comprising a step of mixing the organic-inorganic composite crosslinkable compound (A) with a solvent in an amount of from 0.5 to 10 ml per g of the solid content of the organic-inorganic composite crosslinkable compound (A).

In accordance with an aspect of the present invention, a fuel cell is provided, comprising a proton conducting membrane as mentioned above.

[0034]

[Best Mode for Carrying out the Invention]

The present invention will be described hereinafter with reference to preferred examples, but the present invention is not limited thereto.

[0035]

The proton conducting membrane of the present invention comprises a support filled with a proton conducting structure (β) comprising an acid-containing

structure containing an acid group, in the support structure comprising an organic-inorganic composite structure (α) having a crosslinked structure formed by a metal-oxygen bond, preferably a silicon-oxygen bond and an open-cell structure having internally-formed pores connected continuously to each other by the crosslinked structure.

[0036]

Herein, the proton conducting structure (β) may have an acid group, and an example thereof includes a fluoro-resin-based membrane (Nafion (trade name) membrane (Du Pont Inc.; see US Patent 4,330,654), Dow membrane (Dow Chemical Inc.; see JP-A-4-366137), Aciplex (trade name) membrane (Asahi Kasei Corporation; see JP-A-6-342665), Flemion (trade name) membrane (ASAHI GLASS COMPANY), etc.) comprising a perfluoroalkylene as a main skeleton and having a sulfonic acid group at a portion of the end of perfluorovinylether side chain.

[0037]

In the invention, the proton conducting structure (β) of the invention are used, which includes a crosslinked structure having a metal-oxygen bond represented by a silicon-oxygen bond with acid containing crosslinked structure in the support (α), both of which penetrate each other. Accordingly adhesion of a support

to the proton conducting composition is improved, and the proton conducting membrane, which may not undergo destruction of the interface, even applied with stress between a support and a filling agent due to the change of temperature or differential pressure also during the operation of the fuel cell, may be obtained.

[0038]

That is, since the proton conducting membrane of the invention has a crosslinked structure, the working of the fuel cell in high temperature is stable, and may be used for an extended period of time. Specifically, The crosslinked structure is introduced with sufficient crosslink density, and thus neither great change in dimension nor strength change can be seen, in wet or drying states.

[0039]

The invention includes a crosslinked structure such as metal-oxygen bond, e.g., silicon-oxygen bond, aluminum-oxygen bond, titanium-oxygen bond, zirconium-oxygen bond. Such a crosslinked structure is stable under the circumstance of strong acid, high temperature, and high humidity, and is preferably used as the inner membrane of the fuel cell membrane.

In particular, a silicon-oxygen bond may be easily obtained, and thus particularly preferred for low cost.

[0040]

As the crosslinked structure according to the present invention there may be preferably used a silicon-oxygen bond, but the metal-oxygen bonds other than silicon described above or phosphorus-oxygen bond, boron-oxygen bond, etc. may be used together so far as the cost or ease of producing method cannot be sacrificed. In the case where a metal other than silicon described above is used together, the ratio of the silicon-oxygen bond in the crosslinked structure, normally the atomic ratio of "silicon" to "metals other than silicon" is preferably such that the ratio of silicon atom is 50 mol-% or higher based on 100 mol-% of all the metal atoms.

[0041]

Further, proton conducting membrane of the invention may be provided by using a known method, for example, the following method.

There is a method of producing a proton conducting membrane, where the organic-inorganic composite structure (α) having a crosslinked structure is produced by a step of preparing a mixture containing an organic-inorganic composite crosslinkable compound (A) terminated by at least one crosslinkable silyl group and a carbon atom covalently connected thereto, a step of forming said mixture into a film and a step of subjecting the

crosslinkable silyl group contained in the mixture thus film-formed to hydrolysis and/or condensation; subsequently filling mixture of organic-inorganic composite crosslinkable compound (B) and an acid containing compound (C) in the organic-inorganic composite structure (α) to subject the crosslinkable silyl group contained in the filled mixture to hydrolysis and/or condensation, thereby forming a crosslinked structure of the proton conducting structure (β) in the organic-inorganic composite structure (α).

[0042]

An support as an organic-inorganic composite structure (α) forming the proton conducting membrane of the invention has a crosslinked structure formed by a metal-oxygen bond, preferably silicon-oxygen bond and an open-cell structure having internally-formed pores connected continuously to each other by the crosslinked structure.

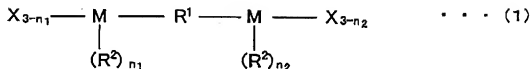
With such structures, all physical properties as well as flexibility can be adjusted also by molecular design between the crosslinked structures.

[0043]

At least one organic-inorganic composite structure (α) is preferably used, which has at least one -O-bond taking part in crosslinking or OH group at both terminals,

and carbon atom covalently connected at -O-bond taking part in crosslinking or OH group, and is represented by the following formula (1), for example.

[chem.9]



(wherein M represents a metal atom; R^1 represents a C_1 - C_{50} carbon atom-containing molecular chain group; R^2 represents a methyl, ethyl, propyl or phenyl group; X represents -O-bond or OH group; and n_1 and n_2 each represent 0, 1 or 2, with the proviso that at least one of n_1 and n_2 represents 1 or 2.)

[0044]

It is necessary that in the formula (1), X represents a bond taking part in crosslinking or a silanol group capable of taking part in crosslinking; n_1 and n_2 each represent any of 0, 1 or 2, with the proviso that at least one of n_1 and n_2 represents 1 or 2, to form an open cell. M represents metal element, and includes various kinds of metal elements such as silicon, zirconium, aluminum, titanium, phosphorus, or boron.

[0045]

Further, in the formula (1), R^1 is a molecular

chain having carbon atoms and is capable of controlling the flexibility and physical properties of the membrane thus obtained. In the case where R^1 is free of carbon atom, the compound thus obtained can be unstable, and on the contrary, when the number of carbon atoms is more than 50, crosslinking is insufficiently made, giving insufficient heat resistance, and R^1 should be a carbon atom-containing molecular chain group having from C_1 to C_{50} .

[0046]

Further, R^1 is preferably a hydrocarbon chain. This is because if R^1 has hetero atoms, the compound can be severed by an acid or heat. On the other hand, R^1 which is a hydrocarbon chain is little subject to attack by an acid, and is a stable compound. Examples of such hydrocarbons include alkylene chains, aromatic group-containing chains, etc. Particularly preferred are straight molecular chains composed of polymethylene chain free of branched chain and are represented by the following formula:

[chem.10]



(wherein m represents an integer of from 1 to 20.)

[0047]

For example, when R^1 has a branched chain, the methine hydrogen in the branched chain is drawn by active radicals developed during operation of fuel cell, and thus is severed by a bond connected between crosslinks.

Further, when R^1 comprises an aromatic compound group, high stability is obtained compared with that having hetero atoms, but decomposition or reaction can occur mainly in the benzyl position as an active point during prolonged use, thus the stability of obtained membrane is deteriorated and is not preferred.

[0048]

R^1 which is a compound group that is a straight polymethylene chain is stable to attack by an acid, radical or the like and thus can be preferably used as a proton conducting membrane for heat-resistant fuel cells.

Further, since the straight polymethylene chain is a flexible structure, the resulting membrane can be provided with a proper flexibility, making it possible to adjust denseness or the like as well. The adjustment of these properties is affected mainly by the molecular length of the polymethylene chain.

[0049]

Accordingly, the polymethylene in the aforementioned formula (5) is preferably in the molecular length (m) of from 1 to 20, and particularly preferred is

methylene chain with m of 8, that is, an octamethylene group. These polymethylene groups can satisfy all the requirements for heat resistance, flexibility and fuel gas barrier properties, but the structure having a molecular length near 10, further easily available materials and 8 methylene side chain is preferred.

[0050]

The organic-inorganic composite structure (α) having Si-O crosslinked structure at both terminals of polymethylene is very stable and useful, as the support of base crosslinked structure of proton conducting membrane for a fuel cell.

[0051]

The organic-inorganic composite structure (α) includes an open-cell structure having pores having an average size of from 0.01 to 10 μm continuously connected therebetween.

Strength of support and volume fraction of the proton conducting composition may be improved by the open-cell structure having such size.

[0052]

Accordingly, such porosity falls within a range of from 20 to 95% by volume, preferably from 50 to 80% in the organic-inorganic composite structure (α) support. When porosity is smaller than such range, the organic-

inorganic composite structure (α) includes only a little proton conducting structure (β) therein. Further, when the porosity is larger than such range, the strength of support is insufficient.

[0053]

The organic-inorganic composite structure (α) may be mixed singly or with a plurality of kinds and used. As described above, when a plurality of the organic-inorganic composite structures (α) is mixed and used, crosslink density can be easily adjusted, making it possible to adjust the porous structure, flexibility, etc. of the membrane. The desired physical properties can be adjusted also by mixing organic-inorganic composite structure (α) having different organic chain lengths, kinds of substituents, etc.

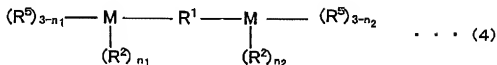
[0054]

When the support of organic-inorganic composite structure (α) forming the proton conducting membrane of the invention is produced, mixture containing the organic-inorganic composite crosslinkable compound (A) is first produced.

The organic-inorganic composite crosslinkable compound (A) preferably employs at least one crosslinkable precursor (A) having at least one crosslinkable silyl group at both terminals and a carbon

atom covalently connected thereto, for example, a crosslinkable precursor (A) represented by the following formula (4).

[chem.11]



(wherein M, R^1 , R^2 , n_1 , and n_2 are the same as the chem.9;; R^5 represents any of Cl, OCH_3 , OC_2H_5 , OC_6H_5 , OH and $OCOCH_3$.)

[0055]

Herein, as the crosslinkable precursor which is the organic-inorganic composite crosslinkable compound (A) and is represented by the formula (4), there may be used one commercially available or one synthesized by the hydrosilylation reaction of hydrolyzable silyl group in a compound having corresponding unsaturated bond.

[0056]

In the formula (4), R^1 is the same as R^1 contained in the organic-inorganic composite structure (α), and similar to function thereof. It is the same that particularly a hydrocarbon group represented by formula (5), and an octamethylene group are preferred.

[0057]

As described above, as a material to introduce a crosslinkable silyl group at both terminals of polymethylene chain, various kinds of bis (hydrolyzable silyl group) polymethylene are known, and for example, polymethylene including ethylene, hexamethylene, octamethylene or nonamethylene are commercially available from Gelest, Inc.

Further, starting materials wherein R^1 corresponds to tetramethylene, decamethylene or tetra decamethylene can be easily synthesized by subjecting materials with unsaturated bond at both terminals, for example, 1,3-butadiene, 1,9-decadiene or 1,13-tetradecadiene to hydrosilylation reaction, and if the polymethylene chain has up to 20 carbon atoms, the crosslinkable precursor (A) can be obtained by subjecting the corresponding diene compound to hydrosilylation reaction.

[0058]

A specific crosslinkable precursor (A), for example, includes bis (diethoxymethylsilyl)ethane, bis(diethoxymethylsilyl) hexane, bis(diethoxymethylsilyl)octane, bis(diethoxymethylsilyl)nonane, bis(dimethylethoxysilyl)ethane, bis(dimethylethoxysilyl)hexane, bis(dimethylethoxysilyl)octane, etc.

[0059]

Further, materials when R^1 has an arylene structure having aromatic ring, for example, bis(trimethoxy silyl ethyl)benzene are commercially available from Gelest, Inc., and corresponding crosslinkable precursor (A) may be easily obtained as a hydrosilylation of divinylbenzen, 1,4' divinyl phenyl, or divinyl naphthalene.

[0060]

The hydrolyzable crosslinking silyl group of the crosslinkable precursor (A) includes an alkoxy silyl group which has alkoxy group such as methoxy, ethoxy, propoxy, or phenoxy directly combined with a silicon atom, a halide silyl group which has halogen such as chlorine connected to silicon atom, or a carboxylated silyl group such as an acetoxy group, etc.

Further, a hydrolyzed silanol group or silanolate group, instead of the hydrolyzable crosslinking silyl group may be used.

[0061]

Further, at least one organic-inorganic composite crosslinkable compound (A) thus obtained is mixed and used, and the materials are mixed with an appropriate solvent as necessary. As the solvent an alcohol such as methanol, ethanol, isopropanol and n-butanol or ether such as tetrahydrofurane and dioxane may be used, but the solvent is not specifically limited so far as

crosslinkable precursor (A) may be solved.

[0062]

Further, the amount of the solvent is from 0.5 to 10 ml, preferably from 1 to 5 ml per g of the solid content in the organic-inorganic composite crosslinkable compound (A) to form an open-cell structure.

In some detail, when the amount of the solvent falls below the above defined range, an open-cell structure can be difficultly formed in the structure (α) thus obtained, and even if an open-cell structure is formed, the porosity is small, and on the contrary, when the amount of the solvent exceeds the above defined range, the crosslinked structure (α) thus obtained can difficultly have an open-cell structure formed therein, and even if an open-cell structure is formed, the structure (α) cannot satisfy the strength required for support.

[0063]

Subsequently, when producing proton conducting membrane, crosslinkable precursor (A) mixture solution obtained at the aforementioned step is formed into film by a known method such as casting method and coating method.

The film-forming method is not specifically limited and may be an arbitrary method so far as a uniform

membrane can be obtained. Further, the thickness of the film thus formed is properly determined by the protonic conductivity, fuel permeability and mechanical strength but is preferably from 10 μm to 1 mm, particularly preferably from 30 to 300 nm as calculated in terms of dried thickness.

[0064]

Subsequently, by subjecting the crosslinkable silyl group contained in the organic-inorganic composite crosslinkable compound (A) thus film-formed to so-called sol-gel reaction, more particularly subjecting the hydrolyzable silyl group in the compound (A) to hydrolysis and condensation or only condensation if the crosslinkable silyl group is a silanol group or silanolate group, a crosslinked structure made of a metal bond such as silicon-oxygen bond is formed to obtain a support (α) which is an organic-inorganic composite. In this case, even if an alkoxide of titanium, zirconium, aluminum or the like is added, hydrolysis or condensation can be conducted by the same reaction.

[0065]

Herein, the open-cell structure having the aforementioned pore diameter and porosity to be formed in the organic-inorganic composite support (α) is formed by making the use of phase separation from the

aforementioned solvent accompanying the increase of the molecular weight of the support by the aforementioned condensation reaction. Accordingly, the formation of the three-dimensional network structure is greatly affected by the percent hydrolysis and concentration reaction rate, and it is necessary that the temperature and catalyst concentration be properly adjusted.

[0066]

In the aforementioned reaction step, the temperature during the formation of the open-cell structure by phase separation after casting is predetermined to be from 5°C to boiling point of solvent, preferably from 10 to 40°C. Subsequently, in order to fixing crosslinking, the material can be cured at a temperature of from boiling point of solvent to 300°C, preferably from 100 to 200°C to obtain a support (α) having a three-dimensional network structure.

[0067]

In the case where the proton conducting membrane of the present invention thus obtained is used at a temperature as high as 100°C or more, it is preferred that the proton conducting membrane be heated to a temperature of not lower than the working temperature to undergo crosslinking. Referring to such heating, the crosslinking step may be effected at a temperature of

from 100 to 300°C or the crosslinking reaction may be effected such that sol-gel curing occurs at a temperature of from 5 to 40°C in 2 hours or more, followed by culturing at a temperature of from 100 to 300°C, preferably from 100 to 200°C, making it possible to fix the crosslinked structure. When the temperature is too low, the crosslinking reaction slows down, and when the temperature is too high, the organic moiety can be deteriorated and it is preferred that heating be effected within the aforementioned temperature range.

Referring to the heating method, known methods such as heating by oven, heating under pressure by autoclave, far infrared ray heating, electromagnetically induced heating and microwave heating may be used singly or in combination.

[0068]

Further, in order to efficiently effect hydrolysis or condensation reaction, the crosslinking reaction may be effected with the crosslinkable precursor mixture solution previously having water incorporated therein or under heating in water vapor.

Further, in order to accelerate the generation of crosslinked structure from the crosslinkable precursor (A), it is preferred that a Brønsted acid such as hydrochloric acid, sulfuric acid and phosphoric acid be

previously added to the reaction system. Further, since the formation of the crosslinked structure can be accelerated also by a base, a base catalyst such as ammonia and sodium hydroxide may be used, but a Brønsted acid catalyst is preferably used to form a crosslinked structure support (α) having a three-dimensional network structure.

[0069]

In the case where the aforementioned Brønsted acid catalyst is used in the form of aqueous solution, the concentration of the aqueous solution is preferably not lower than 5 N to less than 10 N. When the concentration of the aqueous solution falls below this range, the reaction slows down, making it difficult to obtain the desired network structure, and on the contrary, when the concentration of the aqueous solution is not lower than this range, the reaction occurs too rapidly to form the desired network structure to disadvantage.

Further, the added amount of such a Brønsted acid catalyst is preferably such that the relationship represented by the following numerical formula 1 is satisfied.

[0070]

[numerical formula 1]

$$0.5 \leq \frac{z(\sigma c - N_c \times M_c)}{M_s \times 2(3-n)x} \leq 1.5$$

wherein the added amount of γ is x (mol); the number of mols of R^5 is $2(3-n) \times$ (mol); the added amount of catalyst is z (l); the specific gravity of catalyst is σc ; the concentration of catalyst is N_c (normal); the molecular weight of catalyst is M_c ; and the molecular weight of water is M_s .

[0071]

When the added amount of the Brønsted acid catalyst falls below the value satisfying the aforementioned numerical formula 1, the percent hydrolysis is too small, causing the drop of crosslink density, and when the added amount of the Brønsted acid catalyst is greater than this value, the added amount of water increases, making it impossible to form a three-dimensional network structure.

Herein, in the aforementioned numerical formula 1, the numerical values 0.5 and 1.5 each represent the equivalent of water in the aqueous solution of Brønsted acid catalyst to the crosslinkable silyl group, and the numerical value of 1.0 means that water is added in an amount equal to that in the case where all the crosslinking groups are hydrolyzed.

Further, in the aforesaid step of adding a Brønsted acid to accelerate the reaction, when the temperature is

too high, the reaction proceeds too much to handle, and the step is preferably effected at a temperature of not lower than the solidification point of the solvent to lower than the boiling point of the solvent, preferably from 0 to about 40°C.

[0072]

The support (α) membrane thus obtained as a support may be rinsed with metal ion-free water such as distilled water and ion-exchanged water as necessary.

Further, the support (α) membrane thus obtained may be irradiated with ultraviolet rays or electron rays to complete crosslinking, and the obtained support membrane is very flexible.

[0073]

The proton conducting membrane of the present invention comprises the support (α) filled with a proton conducting structure (β) comprising an acid-containing structure containing an acid group, and in some detail, it is a structure having the support (α) and proton conducting structure (β) penetrated by each other.

Since the proton conducting membrane for fuel cell is required to make effective conduction of proton and essentially depends on the concentration of proton in the membrane and the amount and movability of conduction medium (e.g., water), it is preferred that proton be

present in the membrane in a high yield, and to this end, it is necessary that acid groups be disposed in the membrane in an amount as large as possible.

[0074]

When such an acid group is extracted and diffused from the membrane with water supplied into the fuel cell or water or the like produced during the operation of the fuel cell, the concentration of proton in the membrane decreases, resulting in the drop of the protonic conductivity. Thus, it is preferred that the acid be fixed by covalent bonding so that it can be stably present in the membrane over an extended period of time rather than being retained in the membrane by ionic mutual interaction or the like.

[0075]

In the invention, the proton conducting structure (β) may be used various kinds of materials so far as has an acid group, particularly preferably, a structure connected with a compound having an acid group, and metal-oxygen, preferably silicon-oxygen crosslink covalently connected thereto, is preferred.

In other words, with regard to organic-inorganic composite structure (βB) having a structure similar to base structure of the membrane, stable protonic conductivity over an extended period of time may be

secured by strongly connecting an acid with covalent connection.

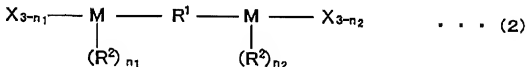
Herein, a metal is specifically limited in a metal-oxygen bond, and is the same in an organic-inorganic composite structure (α).

[0076]

particularly, the proton conducting composition of the invention is used by incorporating organic-inorganic composite structure (β) which may provide heat resistance or flexibility, with acid-containing compound (βC), thereby having heat resistance, and good membrane physical properties such as flexibility, and thus acid may be stably in membrane.

Herein, it is used that the organic-inorganic composite structure (βB) used by incorporating with acid-containing compound (βC) is represented by the following formula (2):

[chem.12]



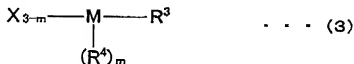
(wherein M represents a metallic atom; X represents -O-bond taking part in crosslinking or OH group; R^1 represents a C_1 - C_{50} carbon atom-containing molecular chain

group; R^2 represents any of methyl, ethyl, propyl and phenyl groups; and n_1 and n_2 each represent 0, 1 or 2.)

[0077]

Further, acid-containing structure (βC) is, not structurally limited thereto so far as connects with crosslinked structure of membrane with and Si-O bond, and it has an acid group, and for example, the structure represented by following formula (3) is preferred.

[chem.13]



(wherein M represents a metal atom; X represents - O-bond taking part in crosslinking or OH group; R^3 represents a molecular chain group having at least one acid group; R^4 represents any of methyl, ethyl, propyl and phenyl groups; and m represents 0, 1 or 2.)

[0078]

Herein, R^3 has at least one acid group, and is the group connected to crosslink group by covalent bond. While an acid group includes various kinds of acids such as sulfonic acid, phosphonic acid, carboxylic acid, sulfuric acid, phosphoric acid, or boric acid may be used, sulfonic acid, which has a low pKa value, can

sufficiently assure the proton concentration in the membrane and is thermally stable, is particularly preferably used.

[0079]

Further, acid-containing structure (βC) is, not particularly limited, so far as it has sulfonic acid, and structure connected to Si-O crosslink, and for example the structure represented by following formula (6) is preferred.

[Chem.14]



(wherein n represents an integer of from 1 to 20.)

[0080]

Herein, the structure comprising a sulfonic acid and a crosslinked structure connected to each other is not specifically limited, but since this structure needs to be excellent in heat resistance, acid resistance, oxidation resistance, etc. because of the object of the present invention, for example, the structure can be the polymethylene chain shown in the formula (5).

Herein, it is preferred that the polymethylene chain be not branched and the sulfonic acid group be present at the end of the polymethylene chain.

This is because when the polymethylene chain is

branched, the methine structure in the branched portion is susceptible to oxidation or radical reaction, and as a result, the sulfonic acid is diffused from the membrane. Furthermore, even if a sulfonic acid is present in the middle of the polymethylene chain rather than at the end of the polymethylene chain, the sulfonic acid-connected portion becomes a methine structure, causing the separation or diffusion of sulfonic acid by the oxidation or the like.

[0081]

Further, the structure having sulfonic acid and crosslinked structure connected to each other is preferably free of aromatic ring. This is because the directly sulfonated aromatic compound can be easily synthesized, but has a disadvantage that it can be easily separated in an opposite manner, and when the fuel cell is subjected to operation under the high temperature and humidity conditions, which is an object of the present invention, a desulfonation reaction can easily occur, causing the deterioration of conductivity.

[0082]

Further, a method which prepares a sulfone group from an aromatic ring via several methylene chains by the addition of a compound such as 1,3-propanesulfon rather than direct sulfonation is known (Ogata et al., "Polymer

Preprint, Japan", 46 (1997), page 1,867), but the methylene adjacent to the aromatic ring becomes an active site called benzyl position, causing the separation of acid by decomposition or the like with the benzyl position as a starting point, and as result, it is much likely that the protonic conductivity can be drastically lowered, and this is not suitable for the acid-connected structure in the present invention.

[0083]

Accordingly, the acid-containing structure (BC) which is preferably used in the present invention is a structure represented by the aforementioned chemical formula (6).

Further, in the aforementioned chemical formula (6), n is preferably from 1 to 20, more preferably from 1 to 12.

Those having n of 0, i.e., those having sulfon group directly connected to silicon atom are undesirable because they are susceptible to hydrolysis, and those having n or more than 20 are undesirable because the crosslink density of the membrane is deteriorated.

Among these compounds, trihydroxysilylpropyl sulfonic acid, which is a starting material of the structure having n of 3, can be particularly preferably used because it is commercially available from Gelest,

Inc., and a synthesis method using allyl bromide as a starting material has been established.

[0084]

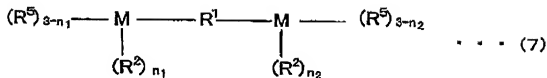
The mixing ratio of the organic-inorganic composite structure (βB) and the acid-containing structure (βC) in the proton conducting structure (β) used in the present invention may be different depending on the chemical structures or the production methods, and the obtained proton conducting membrane is within a range that satisfies the heat resistance, flexibility and the protonic conductivity, there is no particular limit thereon, but when the acid-containing structure (βC) is excessively small, the protonic conductivity becomes extremely low, and thereby, the mixing ratio of the organic-inorganic composite structure (βB) and the acid-containing structure (βC) is preferably in that, generally, the range from 90:10 to 1:99 in the weight ratio, which makes the protonic conductivity compatible with the mechanical property.

[0085]

Furthermore, in order to obtain the organic-inorganic composite structure (βB), an organic-inorganic crosslinkable compound (B) can be used as a starting material. The organic-inorganic crosslinkable compound (B) has the structure represented by the chemical formula

(7).

[Chem.15]

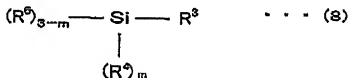


(wherein M, R¹, R², and R⁵ are the same as in the above chemical formula 9, n₁ and n₂ each represent 0, 1 or 2.)

[0086]

On the other hand, in order to obtain the acid-containing structure (βC), the acid-containing compound (C) containing a crosslinkable silyl group and an acid group can be used as a starting material. The acid-containing compound (C) is not particularly limited as long as includes a crosslinkable silyl group, and contains the acid group, but a compound represented by the following formula (8) for example is exemplified.

[Chem.16]



(wherein, R³ represents a molecular chain group having at least one acid group; R⁴ represents methyl,

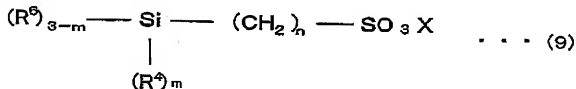
ethyl, propyl or phenyl groups; R^6 represents Cl , OCH_3 , OC_2H_5 , OC_6H_5 , OH , or $OCOCH_3$ group; and m represents 0, 1 or 2.)

[0087]

Furthermore, as the acid group possessed by R^3 there may be used the same acid group as in the aforementioned formula (3), preferably sulfonic acid, which is also thermally stable.

Particularly, When the acid-containing compound (C) has a structure represented by the aforementioned chemical formula (8), the acid-containing compound (C) as a starting material preferably has the structure represented by the following formula (9).

[Chem.17]



(wherein, R^4 represents methyl, ethyl, propyl or phenyl groups; R^6 represents Cl , OCH_3 , OC_2H_5 , OC_6H_5 , OH , or $OCOCH_3$ group; X represents hydrogen, alkali metal, or alkyl group; m represents 0, 1 or 2; and n represents an integer from 1 to 20).

[0088]

Trihydroxysilylpropylsulfonic acid as an acid-

containing compound (C) which is a starting material of the structure of the acid-containing structure (βC) represented by the aforementioned formula (3) wherein n is 3 can be particularly preferably used because it is commercially available from Gelest, Inc. and thus is easily available, and besides this compound, compounds disclosed in JP-A-54-138522 (US Patent 4,152,165) can be preferably used as the acid-containing compound (C).

[0089]

Next, a mixture of the organic-inorganic crosslinkable compound (B) and the acid-containing compound (C) is prepared. Here, any methods may be used which may be a method in which the mixture of the organic-inorganic crosslinkable compound (B) and the acid-containing compound (C) is casted on the support (α) obtained as above, or a method in which the support (α) is dipped in the mixture of the organic-inorganic crosslinkable compound (B) and the acid-containing compound (C), as long as the proton conducting composition (β) can be filled in the support (α).

[0090]

Furthermore, it is preferable that the mixing weight ratio of the organic-inorganic composite crosslinkable compound (B) and the acid-containing compound (C) is within the range of from 90:10 to 1:99 in

the weight ratio.

If the organic-inorganic composite crosslinkable compound (B) is less than 1 part by weight in the mixture, the membrane becomes fragile and the treatment becomes difficult, however, on the other hand, if the organic-inorganic composite crosslinkable compound (B) exceeds 90%, it is not desirable because a sufficient protonic conductivity cannot be obtained. The combination ratio corresponds to the ratio of the organic-inorganic composite structure (βB) and the acid-containing structure (βC) in the proton conducting membrane obtained nearly finally.

[0091]

In the reaction of the organic-inorganic composite crosslinkable compound (B) and the acid-containing compound (C), acid such as hydrochloric acid, sulfuric acid, phosphoric acid, or the like, inorganic base such as ammonia, sodium hydride, or the like, and organic salt groups such as triethylamine, diethylamine, or the like.

Further, When base catalyst is used in the reaction of the organic-inorganic composite crosslinkable compound (B) and the acid-containing compound (C), the step of neutralizing an excess base with hydrochloric acid or sulfuric acid, etc. may be included.

[0092]

Furthermore, instead of the acid-containing compound (C), mercapto group-containing compound (D) having a crosslinkable silyl group and a mercapto group may be used, and in that case, a process is necessary in which the mercapto group in the obtained crosslinkable body is sulfonated by oxidation.

The mercapto group-containing compound (D) used here is not particularly limited only if it has a mercapto group and the crosslinkable silyl group, and may be used arbitrarily.

[0093]

Furthermore, as a method of oxidating the mercapto group, a general oxidizing agent may be used.

Specifically, oxidizing agents nitric acid, hydrogen peroxide, oxygen, organic peroxide (percarboxylic acid), aqueous bromine, hypochlorite, hypobromite, potassium permanganate and chromic acid may be used.

Referring to the oxidation reaction of mercapto group, etc. with these oxidizing reagents, a known method disclosed in "Jikken Kagaku Koza (Institute of Experimental Chemistry)", 3rd edition, Maruzen, page 1,775 and references cited therein, and organic peracids such as peracetic acid and perbenzoic acid are particularly preferably used because they can be

relatively easily handled and give a good yield in oxidation.

[0094]

In order to protonate the sulfonic acid group in the membrane obtained by oxidation, the membrane may be brought into contact with a strong acid such as hydrochloric acid and sulfuric acid, and in this case, the protonating conditions such as acid concentration, dipping time and dipping temperature are properly determined by the concentration of sulfonic acid group in the membrane, the porosity of the membrane, the affinity of the membrane for acid, etc. Representative examples of this method include a method which comprises dipping the membrane in a 1 N sulfuric acid at 50°C for 1 hour, etc.

Furthermore, instead of the acid-containing compound (C), a polysulfide group-containing compound (E) having a crosslinkable silyl group and a polysulfide group may be used.

[0095]

To obtain the acid-containing structure(β C), a method of forming a membrane using a compound having an alkoxy silyl group and an alkyl halide group and then replacing e halogen with sodium sulfite, a method of replacing halogen with dithiocarbonate to oxidize, a

method of reacting directly sulfite with unsaturated bond after forming membrane with a compound having an alkoxy silyl group and unsaturated bond, or a method of adding a sulfur compound such as thiosulfuric acid to unsaturated bond to subject oxygen reaction may be used.

[0096]

An organic-inorganic composite crosslinkable compound forming proton conducting structure (β) including acid-containing structure containing an acid group thus obtained, and an acid-containing compound are filled in the support (α), subsequently hydrolysis and/or condensation of a crosslinkable silyl group contained in the mixture are/is performed. At this time, a solvent may be used, and the solvent used in an organic-inorganic composite crosslinkable compound (A) may be used as a solvent.

[0097]

As described above, by forming a crosslinked structure of a proton conducting structure (β) in a support (α), the proton conducting membrane of the invention is obtained.

In a crosslinking step of such case, the crosslinking method or crosslinking condition same as a method using the organic-inorganic composite structure (α) describe above may be used.

[0098]

The proton conducting membrane of the invention thus obtained is flexible and has a structure in which proton conducting composition is highly filled and the filled proton conducting composition continuously connected in the thickness direction of membrane, and has excellent proton conductivity.

[0099]

The proton conducting membrane thus obtained shows excellent heat resistance and durability, is an organic-inorganic composite membrane which shows excellent proton conductivity at high temperature, and preferably may be used as proton conducting membrane of a fuel cell. To produce a fuel cell with the conducting membrane of the invention, so called a membrane-electrode assembly junctioned between the membrane and catalyst-supported electrode is produced.

[0100]

The membrane-electrode assembly may be produced by suitably using a known method such as thermal press method, or a method coating proton conducting composition on membrane and/or electrode.

Further, a proton conducting membrane of the invention is not limited to a PEFC, and may be used in a chemical sensor or ion exchange membrane, and the like.

[0101]

[Example]

The present invention will be further described hereinafter in the following examples and comparative examples, but the present invention is not limited thereto. The compounds, solvents, etc. used in the examples and comparative examples were all commercially available products.

[Evaluating method]

(1) Evaluation of physical properties of proton conducting membrane

The measurement of the flexing resistance of the proton conducting membrane was executed according to flexing resistance test method (cylindrical mandrel method as described in JIS K 5600-5-1. Using a Type I mandrel (diameter: 10 mm), the measurements were evaluated according to the following criterion.

O ... No cracks observed

x ... Some cracks observed

[0102]

(2) Evaluation of protonic conductivity of proton conducting membrane

A proton conducting membrane of the present invention was coated with a carbon paste (Conducting Graphite Paint; LADO RESEARCH INDUSTRIES, INC) on the

both surfaces thereof, and then bonded to a platinum plate. Using a Type 1260 electrochemical impedance measuring device (produced by Solatron Inc.), impedance was measured at a frequency of from 0.1 Hz to 100 kHz through these platinum plates to evaluate the protonic conductivity of the ionically-conductive membrane.

In the aforementioned measurement, protonic conductivity was measured on a sample supported in an electrically-insulated sealed container in a water vapor atmosphere (95 to 100%RH) at each of cell temperatures which are varying from room temperature to 160°C by a temperature controller. As representative values, those measured at 60°C and 140°C were presented. In the measurement at 100°C or more, measurement was conducted under pressure in the measuring tank.

[0103]

(3) Evaluation of heat resistance of proton conducting membrane

The proton conducting membrane was heated in an unsaturated water vapor in a 140°C autoclave for 5 hours. The proton conducting membrane thus heated was then subjected to visual evaluation, dimensional measurement and flexing resistance test, and the criterion for evaluation is as follows.

Visual: O ... No change from before test

x ... Fading/deformation occurs

Dimensional change: Percent change (%)

Flexing resistance: Same as in (1)

[0104]

(4) Synthesis of precursor

(Synthesis of bifunctional precursor)

A toluene solution of 11.0 g of 1,7-octadiene (produced by Wako Pure Chemical Industries, Ltd.) and 26.9 g of diethoxymethylsilane (produced by Shin-Etsu Silicone Co., Ltd.) was mixed with 0.05 mmol of a solution of Karstedt catalyst (U.S. Pat. 3,775,452) prepared from chloroplatinic acid (produced by Wako Pure Chemical Industries, Ltd. and divinyl tetramethyl disiloxane (produced by Gelest, Inc.) and then stirred at 30°C in a nitrogen atmosphere overnight. The reaction mixture thus obtained was then purified by distillation to obtain 1,8-bis(diethoxymethylsilyl)octane. The structure was identified by NMR.

(Synthesis of trifunctional precursor)

1,8-Bis(dimethylethoxysilyl)octane was obtained in the same manner as mentioned above except that dimethyl ethoxysilane was used instead of diethoxymethylsilane.

[0105]

(5) Evaluation of electricity generation of fuel cell

The membrane thus obtained was used to prepare a single fuel cell unit. The membrane was provided interposed between gas diffusion electrodes (2.0 mg platinum-loaded product, produced by E-TEK), and the combination was then incorporated in a single cell (membrane area: 5.25 cm²) produced by Electrochem Inc. to prepare a single fuel cell unit. The fuel cell thus obtained was then measured for voltage-current curve with hydrogen and oxygen being introduced therein on the anode and cathode thereof, respectively, and an electronic load being connected to the output thereof.

[0106]

[Example 1]

0.6 g of 1,8-bis(diethoxymethylsilyl)octane and 0.5 g of 1,8-bis(dimethylethoxysilyl)octane were dissolved in 1 ml of isopropanol. 0.22 g of a 7 N hydrochloric acid was added to 1 ml of isopropanol. The two solutions were stirred in combination for scores of seconds, and then poured in a polystyrene disc having an inner diameter of 8.4 cm (produced by YAMAMOTO MFG. CO., LTD.) where it was then cultured at room temperature (20°C) for 60 hours to obtain a white rubbery support. The support was measured for porosity and pore diameter by a porosimeter and for inner structure by SEM, and it was confirmed that an open-cell structure having a porosity of 70 vol-% and an

average pore diameter of 500 nm had been formed.

[0107]

Subsequently, a solution obtained by dissolving 0.7 g of trihydroxysilylpropylsulfonic acid (produced by Gelest, Inc.) and 0.015 g of 1,8-bis(dimethylethoxy silyl)octane in 0.63 ml of isopropanol and a solution obtained by adding 0.14 g of a 10 N hydrochloric acid to 0.63 ml of isopropanol were stirred in combination for several minutes, poured onto a support prepared in a disc where the mixture was then heated to room temperature (20°C) for 60 hours and 80°C in an unsaturated water vapor for 24 hours and in a 150°C oven for 6 hours to obtain a white flexible membrane.

[0108]

Before being measured for the aforementioned properties, the membrane thus obtained was rinsed with 80°C flowing water for 2 hours. The inner structure of this membrane was observed under electron microscope, and as a result, it was confirmed that the open cells having an average pore diameter of 500 nm had been densely filled with a resinous material and there had occurred no exfoliation and cracking on the interface of filler with support.

[0109]

The results of evaluation of the membrane thus

obtained are given below.

<Results>

Flexing resistance test O

60°C conductivity (S/cm) 3.0×10^{-2}

140°C conductivity (S/cm) 4.0×10^{-2}

140°C heat resistance

Visual O

Dimensional change -0.1%

Flexing resistance O

The evaluation of electricity generation is shown in Fig. 1.

[0110]

[Example 2]

A three-dimensional network structure was prepared in the same manner as in Example 1.

Subsequently, a solution obtained by dissolving 0.7 g of 3-mercaptopropyltrimethoxysilane (SILA-ACE S810, produced by Chisso Corporation) and 0.015 g of 1,8-bis(dimethylethoxysilyl)octane in 0.63 ml of isopropanol and a solution obtained by adding 0.14 g of a 10 N hydrochloric acid to 0.63 ml of isopropanol were stirred in combination for several minutes, and then poured onto a support prepared in a disc where the mixture was then cured in the same manner as in Example 1 to form a membrane. This membrane was oxidized in a 1.25 : 1

mixture of acetic acid and hydrogen peroxide (30%) over a hot plate having a predetermined temperature of 80°C for 1 hour, and then rinsed in the same manner as in Example 1.

[0111]

The results of evaluation of the membrane thus obtained are given below.

<Results>

Flexing resistance test O

60°C conductivity (S/cm) 4.1×10^{-2}

140°C conductivity (S/cm) 5.2×10^{-2}

140°C heat resistance

Visual O

Dimensional change -0.1%

Flexing resistance O

The evaluation of electricity generation is shown in Fig. 2.

[0112]

[Comparative Example 1]

Curing was attempted in the same manner as in Example 1 except that 0.65 g of 1,8-bis(triethoxysilyl)octane and 0.45 g of 1,8-bis(dimethylethoxysilyl)octane were used instead of 0.6 g of 1,8-bis(diethoxymethylsilyl)octane and 0.5 g of 1,8-bis(dimethylethoxysilyl)octane and 0.27 g of hydrochloric acid was used. As a result, a white semi-transparent membrane which doesn't

exhibit rubberiness was obtained instead of white rubbery support. This membrane had a porosity of 20% by volume and an average pore diameter of 30 nm. The inner structure of this membrane was observed under electron microscope, and it was then confirmed that pores having a diameter of from 10 to 50 nm had been present in a partial continuity. To this support was added the same conducting agent as in Example 1, and curing and rinsing were effected in the same procedure.

[0113]

The results of evaluation of the membrane thus obtained are given below.

<Results>

Flexing resistance test O

60°C conductivity (S/cm) 5.0×10^{-4}

140°C conductivity (S/cm) 6.0×10^{-4}

140°C heat resistance

Visual O

Dimensional change -0.1%

Flexing resistance O

[0114]

[Comparative Example 2]

Curing was attempted in the same manner as in Example 1 except that 1.1 g of 1,8-bis(triethoxysilyl)octane was used instead of 0.6 g of 1,8-

bis(diethoxymethylsilyl)octane and 0.5 g of 1,8-bis(dimethylethoxysilyl) octane and 0.35 g of hydrochloric acid was used. As a result, a transparent and hard membrane was obtained instead of white rubbery support. The inner structure of this membrane was observed under electron microscope, and it was then confirmed that this membrane is an assembly of particles having a particle diameter of from 10 to 50 nm. To this support was added the same conducting agent as in Example 1, and curing and rinsing were effected in the same procedure.

[0115]

The results of evaluation of the membrane thus obtained are given below.

<Results>

Flexing resistance test x

60°C conductivity (S/cm) 6.0×10^{-5}

140°C conductivity (S/cm) 9.0×10^{-5}

140°C heat resistance

Visual O

Dimensional change 0.0%

Flexing resistance x

electricity generation evaluation

[0116]

[Comparative Example 3]

A commercially available Nafion 117 was evaluated in the same manner as mentioned above.

<Results>

Flexing resistance test O

60°C conductivity (S/cm) 8.0×10^{-2}

140°C conductivity (S/cm) 1.0×10^{-1}

140°C heat resistance

Visual x Much deformation

Dimensional change 50%

Flexing resistance O

[0117]

As can be seen in the results above, it was found that when a support made of a crosslinked structure having a specific organic-inorganic composite structure and comprising an open-cell structure having pores having a size of from about 0.01 to 10 μm continuously connected thereto is filled with a proton conducting composition, a proton conducting membrane having unprecedentedly excellent durability, dimensional stability, fuel barrier properties and other properties can be obtained. Further, when the aforementioned support is filled with a proton conducting composition made of the same elements as the support and composed of a crosslinked structure having a specific organic-inorganic composite structure and an acid-containing crosslinked structure, both a high

protonic conductivity and a high heat resistance can be attained at the same time.

[0118]

In the evaluation of heat resistance at 140°C (evaluation 3) in particular, the proton conducting membrane undergoes little deformation or other defects and thus is extremely good. It was further confirmed that the use of the membrane of the present invention makes it possible to make electricity generation by fuel cell.

As can be also seen in the evaluation of electricity generation, the membrane of the present invention is provided with gas barrier properties.

[0119]

It is apparent that these properties are made possible only when the membrane comprises both the organic-inorganic composite structure (α) and the proton conducting structure (β) incorporated therein and no protonic conductivity cannot be obtained when the membrane comprises only the three-dimensional network structure (α) made of organic-inorganic composite structure incorporated therein, though not described in the comparative examples. Further, the membrane comprising only the proton conducting structure (β) containing an acid-containing structure incorporated

therein is relatively brittle and thus can be continuously or discontinuously used over an extended period of time.

[0120]

Accordingly, the constitution that a support made of an organic-inorganic composite structure (α) having a crosslinked structure formed by a metal-oxygen bond and an open-cell structure having internally-formed pores connected continuously to each other by the aforesaid crosslinked structure is filled with a proton conducting structure (β) comprising an acid-containing structure containing an acid group, which is a requirement of the present invention, is essential for high temperature durability fuel cells. By satisfying this requirement, a self-supporting membrane which exhibits a stable protonic conductivity from low temperature to high temperature and can be bent can be obtained.

[0121]

On the other hand, the fluorine-based membrane which has been heretofore used as a representative electrolyte membrane exhibits a high initial conductivity and a relatively good conductivity even after high temperature durability test but undergoes drastic irreversible deformation after high temperature durability test and becomes hard and brittle when dried

and it is thus apparent that the conventional membrane cannot be used as it is for high temperature-working PEFC.

[0122]

[Advantage of the Invention]

The proton conducting membrane of the present invention, has excellent heat resistance, durability, dimensional stability, fuel barrier properties, flexibility, etc. and can be used in high temperature, the working temperature of recently attracting PEFC may increase 100°C or more in a fuel cell using a proton conducting membrane.

As a result, an increase in electricity generating efficiency, and reduction in catalyst CO poisoning are attained. Further, the increase of working temperature is considered by developing cogeneration due to thermal use, and is expected to greatly increase energy efficiency.

[0123]

Further, a method of the producing proton conducting membrane of the invention economically and efficiently can produce the proton conducting membrane of the invention.

[Brief Description of the Drawings]

Fig. 1 is a diagram illustrating the voltage-current curve of a fuel cell comprising an example of the

proton conducting membrane of the present invention, and

Fig. 2 is a diagram illustrating the voltage-current curve of a fuel cell comprising another example of the proton conducting membrane of the present invention.

[Designation of Document] ABSTRACT

[Abstract]

[Task] It is intended to provide a proton conducting membrane which is excellent in heat resistance, durability, dimensional stability, fuel barrier properties, flexibility, etc. and exhibits an excellent protonic conductivity even at high temperatures, a method of producing the same and a fuel cell which can operate stably at high temperatures.

[Means for Resolution] The proton conducting membrane comprises a support filled with a proton conducting structure (β) comprising an acid-containing structure containing an acid group, a support being made of an organic-inorganic composite structure (α) having a crosslinked structure formed by a metal-oxygen bond and an open-cell structure having internally-formed pores connected continuously to each other by the crosslinked structure, and the use of this proton conducting membrane makes it possible to obtain a fuel cell having an excellent performance.

[Selected Drawing] None

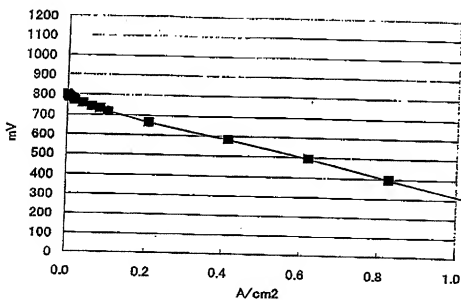
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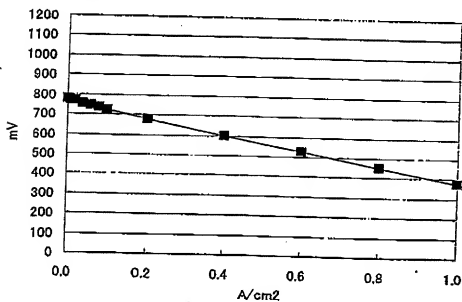
[Designation of Document]

[書類名] 図画 Figure

[図1] [Fig.1]



[図2] [Fig.2]



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